Rapidly disintegrating laundry or detergent mouldings, especially easily handled and dosed tablets - contain granular disintegrating agent with high water adsorption, useful as laundry, dishwashing, stain-removing and water-softening tablet

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• **Abstract :**

DE19710254 A In laundry or detergent mouldings containing disintegrating agent(s) (I) with high water adsorption capacity to increase the porosity or capillarity of the mouldings, especially tablets, (I) is present in a (co)granulate containing at least 20 wt.% (I) and the particle size distribution is such that the dust fraction is not more than 1 wt.% and the total < 0.2 mm is < 10 wt.%.

Also claimed are (i) a method of making the mouldings by mixing the granules and other ingredients in dry form and then moulding, especially pressing to tablets; and (ii) the use of (I) in such mouldings.

USE - The mouldings are used in domestic washing machines, especially in a process in which they are introduced via a dispenser (all claimed). In general, they are useful as laundry agent, dish-washing, stain-removing salt and water-softening tablets in the home, especially in machines.

ADVANTAGE - Tablets are easier to handle and dose than powders and need less packaging volume. On the other hand, they do not disintegrate and dissolve so quickly and there is a risk of residues after washing, especially on textiles. In the finely-divided form normally used in pharmaceuticals, (I) give some improvement but often not enough, especially in tablets containing sticky organic substances, e.g. anionic and/or nonionic surfactants. In contrast, (co)granules are very effective. (Dwg.0/0)

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Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Wasch- oder reinigungsaktive Formkörper für den Gebrauch im Haushalt

(57) Wasch- oder reinigungsaktive Formkörper, insbesondere Tabletten wie Waschmitteltabletten, Geschirrspülmitteltabletten, Fleckensalztabletten oder Wasserenthärtungstabletten, weisen eine für den Gebrauch in Haushaltsmaschinen erforderliche gute Zerfallsgeschwindigkeit auf, wenn sie herkömmliche Sprengmittel, welche aus der Pharmazie bekannt und in der Lege sind, die Porosität bzw. Kapillarität der Formkörper zu erhöhen und ein hohes Adsorptionsvermögen für Wasser besitzen, in einer speziellen Form enthalten.
Dabei liegt das Sprengmittel in grenulerer und gegebenenfalls cogrenulierter Form in dem Formkörper vor, wobei des Sprengmittelgrenulet des Sprengmittel zu mindestens 20 Gew.-% enthält und die Partikelgrößenverteilung (Siebenelyse) derert gesteltet ist, daß maximel 1 Gew.-% an Staubanteilen vorliegen und insgesemt weniger als 10 Gew.-% der Sprengmittelgranulete kleiner els 0,2 mm sind.

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dere der Tabletten, liegt dabei vorzugsweise bei 15 bis 60 g und insbesondere bei 25 bis 40 g pro Formkörper bzw. Tablette; die Stoffdichte der Formkörper bzw. Tabletten weist hingegen üblicherweise Werte oberhalb von 1 kg/dm^3, vorzugsweise von 1,1 bis 1,4 kg/dm^3 auf. Je nach Art der Anwendung, des Wasserhärtebereichs oder der Verschmutzung können 1 oder mehrere, beispielsweise 2 bis 4 Formkörper, insbesondere Tabletten, eingesetzt werden. Weitere erfindungsgemäße Formkörper können auch kleinere Durchmesser bzw. Abmessungen, beispielsweise um 10 mm, aufweisen.

Unter einem homogenen Formkörper werden derartige verstanden, in denen die Inhaltsstoffe des Formkörpers homogen verteilt sind. Unter heterogenen Formkörpern werden dementsprechend solche verstanden, die keine homogene Verteilung ihrer Inhaltsstoffe aufzuweisen haben. Heterogene Formkörper können beispielsweise dadurch hergestellt werden, daß die verschiedenen Inhaltsstoffe nicht zu einem einheitlichen Formkörper, sondern zu einem Formkörper verpreßt wird, der mehrere Schichten, also mindestens zwei Schichten aufweist. Dabei ist es auch möglich, daß diese verschiedenen Schichten unterschiedliche Zerfalls- und Lösegeschwindigkeiten aufweisen. Hieraus können vorteilhafte anwendungstechnische Eigenschaften der Formkörper resultieren. Falls beispielsweise Inhaltsstoffe in den Formkörpern enthalten sind, die sich wechselseitig negativ beeinflussen, so ist es möglich, die eine Komponente in der schneller zerfallenden und schneller löslichen Schicht zu integrieren und die andere Komponente in eine langsamer zerfallende Schicht einzuarbeiten, so daß die erste Komponente mit Vorlaufzeit wirken kann oder bereits abreagiert hat, wenn die zweite in Lösung geht. Der Schichtaufbau der Formkörper kann dabei sowohl stapelartig erfolgen, wobei ein Lösungsvorgang der inneren Schicht(en) an den Kanten des Formkörpers bereits dann erfolgt, wenn die äußeren Schichten noch nicht vollständig gelöst oder zerfallen sind; es kann aber auch eine vollständige Umhüllung der inneren Schicht(en) durch die jeweils weiter außen liegenden Schichten erreicht werden, was zu einer Verhinderung der frühzeitigen Lösung von Bestandteilen der inneren Schicht(en) führt.

In einer weiteren bevorzugten Ausführungsform der Erfindung besteht eine Tablette aus mindestens drei Schichten, also zwei äußeren und mindestens einer inneren Schicht, wobei mindestens in einer der inneren Schichten ein Peroxy-Bleichmittel enthalten ist, während bei der stapelförmigen Tablette die beiden Deckschichten und bei der hüllenförmigen Tablette die äußersten Schichten jedoch frei von Peroxy-Bleichmittel sind. Ebenso ist es möglich, Peroxy-Bleichmittel und gegebenenfalls vorhandene Bleichaktivatoren oder Bleichkatalysatoren und/oder Enzyme räumlich in einer Tablette 1 einem Formkörper voneinander zu trennen. Derartige Ausgestaltungen weisen den Vorteil auf, daß selbst in Fällen, bei denen der Waschmittel- oder Bleichmittel-Formkörper 1 die Waschmittel- oder Bleichmittel-Tablette im direkten Kontakt zu den Textilien in die Waschmaschine oder ins Handwaschbecken gegeben wird, keine Verfleckungen ("spotting") durch Bleichmittel und dergleichen auf den Textilien zu befürchten wären.

Weitere Beispiele für heterogene Formkörper können beispielsweise den europäischen Patentanmeldungen EP-A-0 711 827, EP-A-0 711 828 und EP-A-0 716 144 entnommen werden.

Gemäß der obengenannten Definition können eine Reihe von Sprengmitteln einzeln oder in Kombination, in einem Sprengmittelgranulat oder in verschiedenen Sprengmittelgranulaten vorliegend, eingesetzt werden. Falls verschiedene Sprengmittelgranulate eingesetzt werden sollten, so ist es bevorzugt, daß mehr als 40 Gew.-%, vorzugsweise mindestens 50 Gew.-% und insbesondere mindestens 60 Gew.-%, jeweils bezogen auf die Gesammenge der eingesetzten Sprengmittelgranulate, eine Zusammensetzung und Partikelgrößenverteilung der oben angegebenen Art aufweisen. Da aber gerade die gröber als herkömmlich eingestzte Art der Sprengmittel die Beschleunigung des Zerfalls des wasch- oder reinigungsaktiven Formkörpers bewirkt, ist es besonders vorteilhaft und in hohem Maße wünschenswert, daß auch die Gesamtmenge der verschiedenen Sprengmittelgranulate die obengenannten Merkmale aufweisen.

Zu den bevorzugten Sprengmitteln, welche in granulare bzw. in cogranulierte Form zu überführen sind, zählen Stärke und Stärke-Derivate, Cellulose und Cellulosederivate, beispiels-weise mikrokristalline Cellulose, CMC, MC, Alginsäure und deren Salze, Carboxylmethylamylopectin, Polyacrylsäure, Polyvinylpyrrolidon und Polyvinylpolypyrrolidon. Die Sprengmittelgranulate können auf herkömmliche Art und Weise, beispielsweise durch Sprühtrocknung oder Heißdampftrocknung wäßriger Zubereitungsformen oder durch Granulierung, Pelletierung, Extrusion oder Walzenkompaktierung hergestellt werden. Dabei kann es von Vorteil sein, den Sprengmitteln Zuschlagsstoffe, Granulierhilfsmittel, Träger oder Kaschiermittel der bekannten Art zuzusetzen (cogranulierte Form). Zuschlagsstoffe sind in einer bevorzugten Ausführungsform der Erfindung nicht-tensidische Wirksubstanzen von Wasch- oder Reinigungsmitteln, insbesondere Bleichaktivatoren und/oder Bleichkatalysatoren. Besonders bevorzugt ist dabei ein Sprengmittelgranulat, welches als Zuschlagsstoff Tetraacetylethylendiamin (TAED) und/oder andere Bleichaktivatoren der gängigen Art enthält. Derartige Sprengmittelgranulate können vorteilhafterweise durch Cogranulation des Sprengmittels mit dem Zuschlagsstoff hergestellt werden. Durch eine derartige Cogranulation kann die Verteilung des Sprengmittels in dem Formkörper, insbesondere in der Tablette, vergrößert werden, was in bestimmten Fällen ebenfalls zu einer Verbesserung der Zerfallsgeschwindigkeit des Formkörpers führen kann.

In einer Ausführungsform der Erfindung beträgt der Gehalt der Sprengmittelgranulate an den eigentlichen Sprengmitteln vorzugsweise 50 bis 100 Gew.-%, insbesondere mindestens 70 Gew.-%, wobei Ausgestaltungen mit mindestens 80 oder sogar 90 Gew.-% und darüber besonders vorteilhaft sein können. Auch Sprengmittelgranulate, welche nahezu vollständig aus den handelsüblichen Sprengmitteln hergestellt werden und welche die handelsüblichen Sprengmittel zwischen 97 und 100 Gew.-% enthalten, sind möglich.

In einer weiteren bevorzugten Ausführungsform der Erfindung, in der das Sprengmittel in cogranulierter Form, insbesondere in Kombination mit TAED, in den Sprengmittelgranulaten eingesetzt wird, beträgt der Gehalt an Sprengmittel in dem Granulat mehr als 20 Gew.-% und weniger als 70 Gew.-%, wobei die Restbestandteile vorteilhafterweise zu mindestens 70 Gew.-%, insbesondere zu 80 bis 100 Gew.-%, jeweils bezogen auf die Restbestandteile in dem Sprengmittelgranulat, aus den Wirksubstanzen wie Bleichaktivator, insbesondere TAED, und/oder Bleichkatalysator bestehen.

Falls bei der Herstellung der Sprengmittelgranulate Feinanteile unterhalb 0,2 mm anfallen sollten, so ist es nicht nur bevorzugt, diese soweit abzutrennen, daß die Sprengmittelgranulate weitgehend frei von Staubanteilen sind, worunter im Rahmen dieser Erfindung Partikel mit Partikelgrößen von kleiner als 0,1 mm angesehen werden (siehe oben), sondern auch daß der Gehalt an Partikeln unter 0,2 mm insgesamt auf 0 bis 5 Gew.-% minimiert wird. In einer weiteren

bevorzugten Ausführungsform weisen mindestens 90 Gew.-% der Sprengmittelgranulate eine Partikelgröße von mindestens 0,3 mm und maximal 3 mm, insbesondere bis maximal 2 mm auf.

In einer bevorzugten Ausführungsform beinhalten die erfindungsgemäßen Formkörper Sprengmittelgranulate in Mengen von 1 bis 20 Gew.-%, vorzugsweise von 2 bis 15 Gew.-%, wobei Mengen bis 10 Gew.-% besonders bevorzugt sind.

In einer weiteren bevorzugten Ausführungsform sieht die Erfindung vor, daß nicht nur die Sprengmittelgranulate, sondern auch die restlichen Bestandteile des Formkörpers überwiegend in einer partikulären Form der bereits angegebenen Art vorliegen. So ist es bevorzugt, daß mindestens 50 Gew.-% der restlichen Bestandteile und vorzugsweise mindestens 70 Gew.-% eine Partikelgrößenverteilung zwischen 0,2 und 3 mm aufweisen. Auch hier gilt insbesondere, daß die restlichen Bestandteile Partikel einer Größe von kleiner als 0,2 mm lediglich zu 0 bis 5 Gew.-% enthalten sollen, wobei es besonders vorteilhaft ist, wenn mindestens 90 Gew.-% der sonstigen Bestandteile Partikelgrößen zwischen 0,2 und 3,0 mm aufweisen. Staubanteile sollen soweit wie möglich auch bei den restlichen Bestandteilen vermieden werden. Dies wird beispielsweise dadurch verwirklicht, daß die restlichen Bestandteile in granularer Form vorliegen und/oder in einem oder mehreren Compounds zusammengefaßt sind, welche auf herkömmliche Weise, beispielsweise durch Sprühtrocknung, Heißdampftrocknung, Granulierung/Agglomerierung, Wirbelschichtgranulierung, Walzenkompaktierung, Pelletierung oder Extrusion, hergestellt werden können. Gegebenenfalls bei der Herstellung dieser Compounds anfallende Feinanteile von Partikelgrößen kleiner 0,2 mm werden dabei vorzugsweise vor dem Vermischen mit den Sprengmittelgranulaten entfernt. Ausdrücklich nicht in die Bilanz der Partikelgrößenverteilung der restlichen Bestandteile gehen Oberflächenbehandlungsmittel wie Puderungsmittel ein, die bekanntermaßen sehr feinteilig sind und gerade nicht in grobkörniger Form eingesetzt werden. Sowohl Sprengmittelgranulate als auch restliche Bestandteile können mit diesen festen, feinteiligen Oberflächenbehandlungsmitteln nachbehandelt sein.

Als restliche Bestandteile kommen alle üblichen Inhaltsstoffe von Wasch- oder Reinigungsmitteln, Vorbehandlungsmitteln, Bleichmitteln und Wasserenthärtern in Betracht. In erster Linie zählen hierzu an ionische, nichtionische, kationische, amphotere und zwitterionische Tenside, anorganische und organische, wasserlösliche oder wasserunlösliche Buildersubstanzen und Cobuilder, Bleichmittel, insbesondere Peroxybleichmittel, aber auch Aktivchlorverbindungen, welche vorteilhafterweise umhüllt sind, Bleichaktivatoren und Bleichkatalysatoren, Enzyme und Enzymstabilisatoren, Schauminhibitoren, Vergrauungsinhibitoren, Substanzen, welche das Wiederanschmutzen von Textilien verhindern, sogenannte soil repellents, sowie übliche anorganische Salze wie Sulfate und organische Salze wie Phosphonate, optische Aufheller und Farb- und Duftstoffe. In maschinellen Geschirrspülmitteln ist zusätzlich der Einsatz von herkömmlichen Silberschutzmitteln empfehlenswert.

Zu den bevorzugten anionischen Tensiden zählen sowohl solche auf petrochemischer Basis wie Alkylbenzolsulfonate und Alkansulfonate und Alkyl(ether)sulfate mit ungeraden Kettenlängen als auch solche auf nativer Basis, beispielsweise Fettalkylsulfate oder Fettalkyl(ether)sulfate, Seifen, Sulfosuccinate etc. Besonders bevorzugt sind – gegebenenfalls in Kombination mit geringen Mengen an Seife – Alkylbenzolsulfonate und/oder verschiedene Kettenschnitte von Alkylsulfaten bzw. Alkylethersulfaten. Während bei Alkylbenzolsulfonaten C11-C13-Alkylbenzolsulfonat und C12-Alkylbenzolsulfonat bevorzugt sind, umfassen bei den Alkyl(ether)sulfaten bevorzugte Kettenschnitte C12 bis C16, C12 bis C14, C14 bis C16, C16 bis C18 oder C11 bis C15 bzw. C13 bis C15.

Zu den bevorzugten nichtionischen Tensiden zählen insbesondere die mit durchschnittlich 1 bis 7 Mol EO pro Mol Alkohol ethoxylierten C12-C18-Fettalkohole und die entsprechenden C11-C17-Alkohole, insbesondere C13-C15-Alkohole, aber auch die aus dem Wasch- oder Reinigungsmittelbereich bekannten höher ethoxylierten Alkohole der angegebenen Kettenlänge, Aminoxide, Alkylpolyglykoside. Polyhydroxyfettsäureamidc, Fettsäuremethylesterethoxylate und Gemini-Tenside.

Als bevorzugt eingesetzte anorganische Builder kommen insbesondere herkömmliche Phosphate, mit Bevorzugung des Tripolyphosphats, Zeolithe, wobei besonders Zeolith A, Zeolith P, Zeolith X und beliebige Mischungen aus diesen eine Rolle spielen, aber auch Carbonate, Hydrogencarbonate sowie kristalline und amorphe Silikate mit Sekundärwaschvermögen in Betracht. Zu den üblichen Cobuildern zählen vor allem (co-)polymere Salze von (Poly-)Carbonsäuren, beispielsweise Copolymere der Acrylsäure und der Maleinsäure, aber auch Polycarbonsäuren und deren Salze wie Citronensäure, Weinsäure, Glutarsäure, Bernsteinsäure, Polyasparagінsäure etc. Der Fachmann kennt die einsetzbaren organischen Cobuilder aus unzähligen Veröffentlichungen auf dem Wasch- und Reinigungsmittelgebiet.

Als Bleichmittel werden vor allem die zur Zeit gängigen Peroxybleichmittel wie Perborat und Percarbonat, vor allem auch in Kombination mit den gängigen Bleichaktivatoren und Bleichkatalysatoren, insbesondere auf dem Gebiet der Geschirrspülmittel aber auch die bereits weiter oben genannten Aktivchlorverbindungen eingesetzt.

Bei den Enzymen sind nicht nur Proteasen sondern auch Lipasen, Amylasen, Cellulasen und Peroxidasen sowie beliebige Kombinationen dieser Enzyme von besonderem Interesse.

In einer bevorzugten Ausführungsform der Erfindung werden Aniontensid-haltige Compounds eingesetzt, welche verschiedene Aniontenside – beispielsweise Alkylsulfate und Alkylbenzolsulfonate und/oder Seife oder aber Alkylsulfate und sulfierte Fettsäureglycerinester – und/oder Aniontenside in Kombination mit Nichtensiden, beispielsweise Alkylsulfate verschiedener Kettenlänge, gegebenenfalls auch mehrere Typen von Alkylsulfaten mit verschiedenen Kettenschnitten in Kombination mit ethoxylierten Alkoholen und/oder anderen obengenannten nichtionischen Tensiden enthalten. Beispielsweise können auch anionische und nichtionische Tenside überwiegend in zwei verschiedenen Compounds untergebracht sein.

In einer weiteren bevorzugten Ausführungsform der Erfindung werden mindestens 50 Gew.-%, vorzugsweise 60 bis 100 Gew.-% der restlichen Bestandteile vor dem Vermischen mit den Sprengmittelgranulaten nachbehandelt, d. h. unter granulierenden Bedingungen besprüht oder abgepudert, wobei die wasserfreie Nachbehandlung besonders bevorzugt ist. Als bevorzugte flüssige Bestandteile können nichtionische Tenside und/oder Polyethylenglykole genannt werden. Besonders bevorzugt ist aber auch die Nachbehandlung der restlichen Bestandteile mit einer wasserfreien Schmelze von bei Raumtemperatur festen nichtionischen Verbindungen, insbesondere mit Polyethylenglykolen mit relativen Molekülmassen oberhalb von 2000, vor allem zwischen 4000 und 12000. Als Puderungsmittel kommen wie auch bei den Sprengmittelgranulaten vor allem feinteilige Zeolithe, Kieselsäuren, Sulfate, Calciumstearate, Phosphate und/oder Acetate in Betracht. Hierbei ist in einer bevorzugten Ausführungsform der Erfindung darauf zu achten, daß

Staubanteile und Partikel kleiner 0,2 mm vor dem Vermischen mit den Sprengmittelgranulaten möglichst vollständig abgetrennt werden. Die Anmelderin geht davon aus, daß diese an sich bekannte Maßnahme der Oberflächenbehandlung an Anlösen der Partikel in dem Formkörper vor dessen eigentlichen Zerfall verzögert und aus diesem Grund bei der Herstellung von Formkörpern in Kombination mit den Sprengmittelgranulaten einer ganz bestimmten Partikelgrößenverteilung zu den besonders hervorragenden Zerfalleigenschaften der Formkörper in der wäßrigen Flotte beiträgt.

Ebenso kann sich die Erfindung zunutze machen, daß auch Acidifizierungsmittel wie Citronensäure, Weinsäure oder Bernsteinsäure, aber auch saure Salze anorganischer Säuren ("Hydrogensalze"), beispielsweise Bisulfate, vor allem in Kombination mit carbonathaltigen Systemen zu der Verbesserung der Zerfalleigenschaften der Formkörper beitragen kann. Im Rahmen dieser Erfindung ist dann aber vorgesehen, daß auch diese Acidifizierungsmittel in grobkörniger, insbesondere granularer Form, welche möglichst keine Staubanteile aufweisen und in der Partikelgrößenverteilung derjenigen der Sprengmittelgranulate angepaßt sind, vorliegen. Die granularen Acidifizierungsmittel können beispielsweise in Mengen von 1 bis 10 Gew.-% in den Formkörpern enthalten sein.

Wie bereits mehrfach oben erwähnt, weisen die erfindungsgemäßen Formkörper, insbesondere die bisher schlecht zerfallenden und schlecht löslichen Waschmittelformkörper und Bleichmittelformkörper hervorragende Zerfalleigenschaften auf. Dies kann beispielsweise unter kritischen Bedingungen in einer üblichen Haushaltswaschmaschine (Einsatz direkt in der Waschflotte mittels herkömmlicher Dosiervorrichtung, Feinwaschprogramm oder Buntwäsche, Waschtemperatur maximal 40°C) oder in einem Becherglas bei einer Wassertemperatur von 25°C getestet werden. Die Durchführung der entsprechenden Tests wird im Beispielteil beschrieben. Unter diesen Bedingungen zerfallen die erfindungsgemäßen Formkörper nicht nur innerhalb von 10 Minuten vollständig; die bevorzugten Ausführungsformen weisen Zerfallzeiten im Becherglastest von weniger als 3 Minuten, insbesondere von weniger als 2 Minuten auf. Besonders vorteilhafte Ausführungsformen weisen sogar Zerfallzeiten von weniger als 1 Minute auf. Zerfallzeiten von weniger als 3 Minuten im Becherglastest reichen aus, um die Waschmittelformkörper oder die Waschadditivformkörper über die Einspülkammer herkömmlicher Haushaltswaschmaschinen in die Waschflotte einspülen zu lassen. In einer weiteren Ausführungsform der Erfindung wird deshalb ein Waschverfahren beansprucht, wobei der Formkörper über die Einspülvorrichtung der Haushaltswaschmaschine in die Waschflotte eingebracht wird. Die Lösezeiten der Formkörper in der Waschmaschine betragen vorzugsweise weniger als 8 Minuten und insbesondere weniger als 5 Minuten.

Die eigentliche Herstellung der erfindungsgemäßen Formkörper erfolgt zunächst durch das trockene Vermischen der Sprengmittelgranulate mit den restlichen Bestandteilen und anschließendes Informbringen, insbesondere Verpressen zu Tabletten, wobei auf herkömmliche Verfahren (beispielsweise wie in der herkömmlichen Patentliteratur zu Tablettierungen, vor allem auf dem Wasch- oder Reinigungsmittelgebiet, insbesondere wie in den obengenannten Patentanmeldungen und dem Artikel "Tablettierung: Stand der Technik", SÖFW-Journal, 122. Jahrgang, S. 1016–1021 (1996) beschrieben) zurückgegriffen werden kann.

Patentansprüche

1. Wasch- oder reinigungsaktiver Formkörper, enthaltend mindestens ein Sprengmittel, das in der Lage ist, die Porosität bzw. Kapillarität von Formkörpern, insbesondere von Tabletten, zu erhöhen und ein hohes Adsorptionsvermögen für Wasser besitzt, **dadurch gekennzeichnet**, daß dieses Sprengmittel in granularer und gegebenenfalls in cogranulierter Form in dem Formkörper vorliegt, das Sprengmittelgranulat das Sprengmittel oder die Sprengmittel zu mindestens 20 Gew.-% enthält und die Partikelgrößenverteilung (Siebanalyse) derart gestaltet ist, daß maximal 1 Gew.-% an Staubanteilen vorliegen und insgesamt weniger als 10 Gew.-% der Sprengmittelgranulate kleiner als 0,2 mm sind.

2. Mittel nach Anspruch 1, dadurch gekennzeichnet daß das Sprengmittelgranulat das oder die Sprengmittel in Mengen von 25 bis 100 Gew.-% enthält.

3. Mittel, insbesondere Tablette nach Anspruch 1, dadurch gekennzeichnet, daß mindestens 90 Gew.-% der Sprengmittelgranulate eine Partikelgröße von mindestens 0,2 mm und maximal 3 mm aufweisen.

4. Mittel nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Anteil der Sprengmittelgranulate mit einer Partikelgröße kleiner 0,2 mm auf 0 bis 5 Gew.-% minimiert ist, wobei es bevorzugt ist, daß mindestens 90 Gew.-% der Sprengmittelgranulate eine Partikelgröße von mindestens 0,3 mm und maximal 1,6 mm aufweisen.

5. Mittel nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Sprengmittelgranulat das oder die Sprengmittel in Mengen von 50 bis 100 Gew.-%, insbesondere von mindestens 70 Gew.-% enthält.

6. Mittel nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Sprengmittelgranulat in cogranulierter Form vorliegt und der Gehalt des oder der Sprengmittel in dem Sprengmittelgranulat mehr als 20 Gew.-% und weniger als 70 Gew.-% beträgt.

7. Mittel nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß es Sprengmittelgranulate in Mengen von 1 bis 25 Gew.-%, vorzugsweise von 2 bis 15 Gew.-% enthält, wobei Mengen bis 10 Gew.-% besonders bevorzugt sind.

8. Mittel nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß es Zerfallszeiten im Becherglastest (Wassertemperatur 25°C) von weniger als 3 Minuten, insbesondere von weniger als 2 Minuten aufweist und Lösezeiten in der Waschmaschine von weniger als 8 Minuten, insbesondere von weniger als 5 Minuten aufweist.

9. Verfahren zur Herstellung eines wasch- oder reinigungsaktiven Formkörpers, enthaltend mindestens ein Sprengmittel, das in der Lage ist, die Porosität bzw. die Kapillarität von Formkörpern, insbesondere von Tabletten, zu erhöhen und ein hohes Adsorptionsvermögen für Wasser besitzt, wobei dieses Sprengmittel in granularer oder in cogranulierter Form in dem Formkörper vorliegt, das Sprengmittelgranulat das Sprengmittel oder die Sprengmittel zu mindestens 20 Gew.-% enthält und die Partikelgrößenverteilung (Siebanalyse) derart gestaltet ist, daß maximal 1 Gew.-% an Staubanteilen vorliegen und weniger als 10 Gew.-% der Sprengmittelgranulate kleiner als 0,2 mm sind, dadurch gekennzeichnet, daß zunächst das trockene Vermischen der Sprengmittelgranulate mit den restlichen Bestandteilen und anschließend das Informbringen, insbesondere Verpressen zu Tabletten, erfolgt.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß mindestens 50 Gew.-% und vorzugsweise mindestens 70 Gew.-% der restlichen Bestandteile der

Formkörper (unter Ausschluß etwaiger Puderungsmittel) eine Partikelgröße zwischen 0,2 und 3 mm aufweisen.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß die restlichen Bestandteile in granularer Form vorliegen und/oder in einem Compound oder mehreren Compounds zusammengefaßt werden.

12. Verwendung eines Sprengmittels, das in der Lage ist, die Porosität bzw. die Kapillarität von Formkörpern, insbesondere von Tabletten, zu erhöhen und ein hohes Adsorptionsvermögen für Wasser besitzt, in granularer oder in cogranulierter Form in wasch- oder reinigungsaktiven Formkörpern, wobei das Sprengmittelgranulat das Sprengmittel oder die Sprengmittel zu mindestens 20 Gew.-% enthält und die Partikelgrößenverteilung (Siebanalyse) derart gestaltet ist, daß maximal 1 Gew.-% an Staubanteilen vorliegen und weniger als 10 Gew.-% der Sprengmittelgranulate kleiner als 0,2 mm sind.

13. Verwendung eines Waschmittelformkörpers nach einem der Ansprüche 1 bis 8 in Haushaltswaschmaschinen.

14. Waschverfahren unter Verwendung eines Formkörpers nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß der Formkörper über die Einspülvorrichtung der Haushaltswaschmaschine in die Waschflotte eingebracht wird.

- Leerseite -

Household Detergent of Cleaning Action Shaped Bodies

This invention relates to washing- or cleaning-active shapes, above all tablets, such as detergent tablets, dishwasher tablets, stain remover tablets or water softening tablets, for use in the home, more particularly for use in machines, to a process for the production of these shapes and to their use.

Washing- or cleaning-active shapes, more particularly tablets, have a number of advantages over powder-form compositions, including easy handling, simple dosing and low packaging volumes. However, problems arise out of the fact that comparatively high pressures have to be applied in the compression of the powder-form constituents in order to achieve adequate dimensional stability and fracture resistance. On account of the high compression involved, tablets of the type in question often show unsatisfactory disintegrating and dissolving properties in use so that the active substances are reduced too slowly in the washing or cleaning cycle and textiles in particular are in danger of being left with residues after the wash cycle.

The problem of the slow disintegration of tablets has been known for some time, more especially in the pharmaceutical industry. Here, the problem has been overcome or at least eased by the addition of certain disintegration aids known as tablet disintegrators. According to *Römpp (9th Edition, Vol. 6, page 4440)* and *Voigt "Lehrbuch der pharmazeutischen Technologie" (6th Edition, 1987),* tablet disintegrators are auxiliaries which provide for the rapid disintegration of tablets in water or gastric juices and for the release of the pharmaceuticals in an absorbable form. According to their action mechanism, they are classed as substances which increase the porosity or capillarity ("wick effect") of tablets and which have a high

adsorption capacity for water, as gas-evolving substances for effervescent tablets or as hydrophilicizing agents which ensure that the constituent particles of tablets are wetted in water. The first class includes the substances known as traditional disintegrating agents, such as starch, cellulose and cellulose derivatives, alginates, dextrans, crosslinked polyvinyl pyrrolidones and many others while the second class includes systems of weak acids and carbonate-containing agents, more particularly citric acid and tartaric acid in combination with hydrogen carbonate or carbonate. Examples of the third class are polyethylene glycol sorbitan fatty acid esters.

Thus, it is proposed in German patent application **938 566** to convert acetyl salicylic acid before compression into granules and, after complete but careful drying, to coat the granules thus formed with highly disperse silica. The acetyl salicylic acid granules coated with the highly disperse silica powder may then be mixed with other tablet ingredients, which may be present in powder form or granular form, and the resulting mixture is tabletted. The separating layer of highly disperse silica not only acts as an insulating layer and as protection against unwanted reactions, it also contributes towards the rapid disintegration of the tablets, even after prolonged storage.

German patent application **12 28 029** describes a process for the production of tablets in which powder mixtures – without preliminary granulation – are first mixed with cellulose powder and optionally highly disperse silica and the resulting mixture is compressed, in one preferred embodiment after grinding.

According to German patent application **41 21 127**, a particularly effective auxiliary in the production of pharmaceutical tablets contains cellulose particles with a coating material fixed to their surface. The auxiliary is used in the form of fine particles, mean particle sizes below 200 µm being described as particularly advantageous. These fine-particle

auxiliaries, which – in the production of pharmaceuticals – lead to tablets with both a relatively high fracture resistance and a relatively high disintegration rate, are produced in particular by a grinding process carried out in a ball mill.

Accordingly, conventional tablet disintegrators belonging to the first class mentioned above are normally either mixed in very fine-particle form with the other tablet ingredients, which may be present in the form of fine particles or granules, before compression or the other tablet ingredients are coated or powdered/dusted with the tablet disintegrator.

According to the teaching of European patent **EP-B 0 523 099**, disintegrators known from the production of pharmaceuticals may also be used in detergents or cleaning products. The disintegrators mentioned include swellable layer silicates, such as bentonites, natural materials and derivatives thereof based on starch and cellulose, alginates and the like, potato starch, methyl cellulose and/or hydroxypropyl cellulose. These disintegrators may be mixed with, or even incorporated in, the granules to be compressed.

According to International patent application **WO-A-96/06156** also, it can be of advantage to incorporate disintegrators in detergent or dishwasher tablets. Once again, microcrystalline cellulose, sugars, such as sorbitol, and also layer silicates, more particularly fine-particle swellable layer silicates of the bentonite and smectite type, are mentioned as typical disintegrators. Substances which contribute towards gas formation, such as citric acid, bisulfate, bicarbonate, carbonate and percarbonate, are also mentioned as possible disintegration aids.

Although neither of the last two prior-art documents cited above specifies the exact particle size distribution which suitable disintegrators are supposed to have, figures relating to the microcrystallinity of the cellulose and the particle fineness of the layer silicates suggest to the expert, above all in connection with the literature known from the

production of pharmaceutical tablets, that conventional disintegrators are supposed to be used in fine-particle form. This is consistent with the fact that, hitherto, relatively coarse products obtained, for example, by granulation of fine powders, which are expressly marketed as tablet disintegrators, have not been commercially available.

European patent applications **EP-A-0 466 485, EP-A-0 522 766, EP-A-0 711 827, EP-A-0 711 828** and **EP-A-0 716 144** describe the production of cleaning-active tablets in which compacted particulate material with a particle size of 180 to 2000 µm is used. The resulting tablets may have both a homogeneous structure and a heterogeneous structure. According to EP-A-0 522 766, the surfactant- and builder-containing particles at least are coated with a solution or dispersion of a binder/disintegration aid, more particularly polyethylene glycol. Other binders/disintegration aids are the already repeatedly described and known disintegrating agents, for example starches and starch derivatives, commercially available cellulose derivatives, such as crosslinked and modified cellulose, microcrystalline cellulose fibers, crosslinked polyvinyl pyrrolidones, layer silicates, etc. Other suitable coating materials are weak acids, such as citric acid or tartaric acid which, in conjunction with carbonate-containing sources, lead to effervescent effects on contact with water and which, according to Römpp's definition, belong to the second class of disintegrating agents. In these cases, too, no specific details are provided as to the particle size distribution of the disintegrators. However, they are all applied to the surface of granules. This is done either – as mentioned – in liquid to disperse form or in solid form. It is known to the expert in this connection that fine-particle solids, i.e. powder-like solids, which normally also contain relatively high percentages of dust, can be used for coating particles with particulate solids, so-called "powdering".

According to EP-A-0 711 827, the use of particles consisting predominantly of citrate, which has a certain solubility in water, also leads

as a secondary effect to accelerated disintegration of the tablets. It is assumed that the dissolution of the citrate locally increases the ion strength over a transitional period so that the gelling of surfactants is suppressed and, as a result, the disintegration of the tablet is not impeded. According to this patent application, therefore, citrate is not a disintegrating agent in the accepted sense, but acts as an anti-gelling agent.

The proposed solutions mentioned in the foregoing produce the required result in the production of pharmaceutical tablets. Although, in the field of detergents and cleaning products, they contribute towards an improvement in the disintegration properties of washing- or cleaning-active tablets, the improvement achieved is inadequate in many cases. This applies in particular when the percentage of tacky organic substances in the tablets, for example anionic and/or nonionic surfactants, increases. This is one of the reasons why, hitherto, detergent tablets which satisfy stringent consumer requirements have not been commercially available. However, in the field of dishwashing detergents and detergent additives also, tablets do not have a sufficiently high disintegration rate despite an often satisfactory fracture resistance. Increasing the rate at which dishwasher tablets also disintegrate and dissolve can have advantages, particularly for phases which contain active substances that are supposed to be effective at the beginning of the dishwashing process or at relatively low temperatures.

Accordingly, the problem addressed by the present invention was to provide washing- or cleaning-active shapes which would contain a disintegrating agent with a high adsorption capacity for water that would be capable of increasing the porosity or the capillarity of the tablets and which would not have any of the disadvantages mentioned above. Another problem addressed by the invention was to provide a process for the production of these improved washing- or cleaning-active shapes.

It has now been found that the conventional disintegrating agents

known from the production of pharmaceutical tablets lead to rapidly disintegrating washing- or cleaning-active shapes providing they are not used in the usual way.

In a first embodiment, therefore, the present invention relates to a washing- or cleaning-active shape containing at least one disintegrating agent which is capable of increasing the porosity or capillarity of shapes, more particularly tablets, and which has a high adsorption capacity for water, this disintegrating agent being present in the shape in granular and optionally in co-granulated form, the granules of disintegrating agent (disintegrator granules) containing at least 20% by weight and preferably 25 to 100% by weight of the disintegrating agent or – where several disintegrating agents are used – the disintegrating agents and the particle size distribution (sieve analysis) being such that at most 1% by weight, preferably less, of dust-fine particles are present and a total – including any dust-fine particles present – of less than 10% by weight of the disintegrator granules being smaller than 0.2 mm in size. In one advantageous embodiment, at least 90% by weight of the disintegrator granules have a particle size of at least 0.2 mm and at most 3 mm.

In the context of the present invention, disintegrating agents in granular form or in co-granulated form or disintegrator granules are understood to include any disintegrating agents which are present per se in the form of fine-particle powders and which have been converted into coarser particles by spray drying, granulation, agglomeration, compacting, pelleting or extrusion.

A definition of what is meant by washing- or cleaning-active shapes was given earlier on. They are primarily cylindrical objects or tablets which may be used as laundry detergents, dishwashing detergents, bleaching agents (spotting salts) and optionally as pretreatment agents, for example as water softeners or bleaching agents. However, the term "shape" is not confined to tablets and, in principle, encompasses any three-dimensional

form which the starting materials can be made to assume, optionally under the effect of an external container. Cylindrical shapes can have a height which is smaller or greater than or equal to the diameter of the base. However, the shapes may also have a angular base, for example a rectangular base, more particularly a square base, or even a rhombic or trapezoidal base. Other versions include three-cornered or more than four-cornered bases of the shape.

By virtue of the outstanding disintegrating properties of the shapes according to the invention, it is possible, but not absolutely essential, directly to introduce the shapes into the aqueous liquor of a machine washing process by means of a dispenser. It is even possible to place the shape or shapes in the dispensing compartment of commercially available domestic machines, more particularly washing machines. Accordingly, in one preferred embodiment of the invention, the three-dimensional form of the shapes is adapted in its dimensions to the dispensing compartment of commercially available domestic machines.

Another preferred shape has a plate-like or slab-like structure with alternately thick long segments and thin short segments, so that individual segments can be broken off from this "bar" at the predetermined weak spots, which the short thin segments represent, and introduced into the machine or rather into the dispensing compartment of the machine. This "bar" principle can also be embodied in other geometric forms, for example vertical triangles which are only joined to one another at one of their longitudinal sides.

In one preferred embodiment, the invention provides homogeneous or heterogeneous shapes, more particularly tablets, the tablets having a diameter of preferably 20 to 60 mm and, more preferably, of 40±10 mm. The height of these tablets is preferably 10 to 30 mm and more preferably 15 to 25 mm. The weight of the individual shapes, more particularly the tablets, is preferably between 15 and 60 g and more preferably between 25

and 40 g per shape or tablet. By contrast, the density of the shapes or tablets normally assumes values above 1 kg/dm³ and preferably between 1.1 and 1.4 kg/dm³. Depending on the nature of the application, the water hardness range and the degree of soiling, one or more shapes, for example 2 to 4 shapes, more particularly tablets, may be used. Other shapes according to the invention may even have smaller diameters or dimensions, for example of the order of 10 mm.

A homogeneous shape in the context of the present invention is one in which the ingredients of the detergent are uniformly distributed throughout the shape. Accordingly, heterogeneous shapes are shapes in which the ingredients are not homogeneously distributed. Heterogeneous shapes may be produced, for example, by compressing the various ingredients to form a shape comprising several layers, i.e. at least two layers, rather than into a monolayer shape. These various layers may have different disintegration and dissolving rates. This can provide the shapes with favorable performance properties. If, for example, the shapes contain ingredients which adversely affect one another, one component may be integrated in the more quickly disintegrating and dissolving layer while the other component may be incorporated in a more slowly disintegrating layer so that the first component can act in advance or can already have reacted off by the time the second component dissolves. The various layers of the shapes can be arranged in the form of a stack, in which case the inner layer(s) dissolve at the edges of the shape before the outer layers have completely dissolved or disintegrated. Alternatively, however, the inner layer(s) may also be completely surrounded by the layers lying further to the outside which prevents constituents of the inner layer(s) from dissolving prematurely.

In another preferred embodiment of the invention, a tablet consists of at least three layers, i.e. two outer layers and at least one inner layer, a peroxy bleaching agent being present in at least one of the inner layers

whereas, in the case of the stack-like tablet, the two cover layers and, in the case of the envelope-like tablet, the outermost layers are free from peroxy bleaching agent. In another possible embodiment, peroxy bleaching agent and any bleach activators or bleach catalysts present and/or enzymes may be spatially separated from one another in one and the same tablet/shape. Embodiments such as these have the advantage that, even in cases where the shape/tablet of detergent or bleaching agent is introduced into the washing machine or into the hand washing bowl in direct contact with the fabrics, there would be no danger of spotting by bleaching agent or the like on the fabrics.

Other examples of heterogeneous shapes can be found, for example, in European patent applications EP-A-0 711 827, EP-A-0 711 828 and EP-A-0 716 144.

According to the above definition, several disintegrating agents may be used either individually or in combination, being present in the same disintegrator granules or in various disintegrator granules. Where various disintegrator granules are to be used, preferably more than 40% by weight, more preferably at least 50% by weight and, most preferably, at least 60% by weight, based on the total quantity of disintegrator granules used, have a composition and particle size distribution of the type mentioned above. However, since it is precisely the coarser than usual type of disintegrating agent used which accelerates disintegration of the washing- or cleaning-shape, it is of particular advantage, and highly desirable, for all the various disintegrator agent granules used to have the features mentioned above.

Preferred disintegrating agents which have to be converted into granular form or into co-granulated form include starch and starch derivatives, cellulose and cellulose derivatives, for example microcrystalline cellulose, CMC, MC, alginic acid and salts thereof, carboxymethyl amylopectin, polyacrylic acid, polyvinyl pyrrolidone and polyvinyl polypyrrolidone. The disintegrator granules may be conventionally

produced, for example by spray drying or superheated steam drying of aqueous preparations or by granulation, pelleting, extrusion or roll compacting. It can be of advantage to incorporate additives, granulation aids, carriers or coating agents of known types in the disintegrating agents (co-granulated form). In one preferred embodiment of the invention, additives are non-surface-active ingredients of detergents or cleaning compositions, more particularly bleach activators and/or bleach catalysts. Particularly preferred disintegrating agent granules are those which contain tetraacetyl ethylenediamine (TAED) and/or other conventional bleach activators as additives. Disintegrator granules such as these may advantageously be produced by co-granulation of the disintegrating agent with the additive. Co-granulation in this way can increase the distribution of the disintegrating agent in the shape, more especially in the tablet, which in certain cases can also lead to an improvement in the disintegration rate of the shape/tablet.

According to the present invention, it is particularly preferred to use cellulose-containing disintegrating agents of the type described in earlier German patent application **197 09 991.2**. These disintegrating agents are cellulose-containing materials which have been compacted, compacted wood-based materials, such as TMP (thermomechanical pulp) or CTMP (chemothermomechanical pulp) preferably being used. Particularly preferred disintegrating agents such as these are commercially available from the Rettenmaier Company, for example, under the names of Arbocel® B and Arbocel® BC (beech cellulose), Arbocel® BE (beech sulfite cellulose), Arbocel® B-SCH (cotton cellulose), Arbocel® FIC (spruce cellulose) and other Arbocel® types (Arbocel® TF-30-HG).

In one embodiment of the invention, the content of actual disintegrating agents in the disintegrator granules is preferably from 50 to 100% by weight and more preferably at least 70% by weight, embodiments containing at least 80 or even 90% by weight or more being particularly

advantageous. Disintegrator granules which are made almost entirely of the commercially available disintegrating agents, i.e. contain between 97 and 100% by weight of the commercially available disintegrating agents, are also possible.

In another preferred embodiment of the invention in which the disintegrating agent is used in co-granulated form, more especially in combination with TAED, in the disintegrator granules, the content of disintegrating agent in the granules is more than 20% by weight and less than 70% by weight, advantageously at least 70% by weight and more particularly from 80 to 100% by weight of the other constituents, based on the other constituents in the disintegrator granules, consisting of active substances, such as bleach activator, more especially TAED, and/or bleach catalyst.

If fines smaller than 0.2 mm in size should accumulate in the production of the disintegrator granules, not only is it preferred to remove them to such an extent that the disintegrator granules are substantially free from dust (dust in the context of the invention being particles smaller than 0.1 mm in size, see above), but also to such an extent that the total content of particles smaller than 0.2 mm in size is minimized to 0 - 5% by weight. In another preferred embodiment, at least 90% by weight of the disintegrator granules have a particle size of at least 0.3 mm and at most 3 mm, more particularly up to at most 2 mm.

In one preferred embodiment, the shapes according to the invention contain disintegrator granules in quantities of 1 to 20% by weight and preferably in quantities of 2 to 15% by weight, quantities of up to 10% by weight being particularly preferred.

In another preferred embodiment of the invention, not only the disintegrator granules, but also the other constituents of the detergent shape are mainly present in the particulate form mentioned in the foregoing. Thus, preferably at least 50% by weight of the other

constituents and more preferably at least 70% by weight have a particle size distribution of 0.2 to 3 mm. In this case, too, it is particularly important that the other constituents should only contain 0 to 5% by weight of particles smaller than 0.2 mm in size. In one particularly advantageous embodiment, at least 90% by weight of the other constituents have particle sizes of 0.2 to 3.0 mm. In the other constituents also, dust should be avoided as far as possible. This is achieved, for example, by the other constituents being present in granular form and/or being combined in one or more compounds which may be conventionally produced, for example by spray drying, superheated steam drying, granulation/agglomeration, fluidized bed granulation, roll compacting, pelleting or extrusion. Any fines smaller than 0.2 mm in size accumulating in the production of these compounds are preferably removed before mixing with the disintegrator granules. Surface treatment compositions, such as powdering agents, which are known to consist of very fine particles and which are just not used in coarse-particle form, are specifically not included in the overall particle size distribution of the other constituents. Both disintegrator granules and also other constituents may be aftertreated with solid fine-particle surface treatment compositions.

The other constituents may be any typical detergent ingredients, pretreatment compositions, bleaching agents and water softeners. These include above all anionic, nonionic, cationic, amphoteric and zwitterionic surfactants, inorganic and organic, water-soluble or water-insoluble builders and co-builders, bleaching agents, more especially peroxy bleaching agents, and active chlorine compounds which are advantageously coated, bleach activators and bleach catalysts, enzymes and enzyme stabilizers, foam inhibitors, redeposition inhibitors, substances which prevent the resoiling of fabrics, so-called soil repellents, and typical inorganic salts, such as sulfates and organic sulfates, such as phosphonates, optical brighteners and dyes and perfumes. In addition, the

use of conventional silver protectors is recommended for machine dishwashing detergents.

Preferred anionic surfactants include both those based on petrochemicals, such as alkyl benzenesulfonates and alkane sulfonates and alkyl (ether)sulfates with odd chain lengths, and those based on native materials, for example fatty alkyl sulfates or fatty alkyl (ether)sulfates, soaps, sulfosuccinates, etc. Alkyl benzenesulfonates and/or various chain cuts of alkyl sulfates or alkyl ether sulfates are particularly preferred, optionally in combination with small quantities of soap. Whereas, in the case of alkyl benzenesulfonates, C_{11-13} alkyl benzenesulfonate and C_{12} alkyl benzenesulfonate are preferred, preferred chain cuts in the case of the alkyl (ether)sulfates are C_{12} to C_{16}, C_{12} to C_{14}, C_{14} to C_{16}, C_{16} to C_{18} or C_{11} to C_{15} or C_{13} to C_{15}.

Preferred nonionic surfactants include in particular C_{12-18} fatty alcohols ethoxylated with on average 1 to 7 moles of EO per mole of alcohol and the corresponding C_{11-17} alcohols, more particularly C_{13-15} alcohols, and the more highly ethoxylated alcohols with the chain lengths mentioned known from the field of detergents and cleaning compositions, amine oxides, alkyl polyglycosides, polyhydroxyfatty acid amides, fatty acid methyl ester ethoxylates and gemini surfactants.

Preferred inorganic builders are, in particular, conventional phosphates, preferably tripolyphosphate, zeolites, more especially zeolite A, zeolite P, zeolite X and mixtures thereof, and carbonates, hydrogen carbonates and crystalline and amorphous silicates with multiple wash cycle performance. Conventional co-builders include, above all, (co)polymeric salts of (poly)carboxylic acids, for example copolymers of acrylic acid and maleic acid, and also polycarboxylic acids and salts thereof, such as citric acid, tartaric acid, glutaric acid, succinic acid, polyaspartic acid, etc. The expert knows the organic co-builders suitable for use in accordance with the invention from innumerable publications on

the subject of detergents and cleaners.

Suitable bleaching agents are, above all, the peroxy bleaching agents widely used at the present time, such as perborate and percarbonate, above all in combination with conventional bleach activators and bleach catalysts, more especially in the field of dishwashing detergents, and the active chlorine compounds mentioned earlier on.

Among the enzymes, not only proteases, but also lipases, amylases, cellulases and peroxidases and combinations of these enzymes are of particular interest.

A preferred embodiment of the invention is characterized by the use of anionic surfactant-containing compounds in various anionic surfactants – for example alkyl sulfates and alkenyl benzenesulfonates and/or soap or even alkyl sulfates and sulfonated fatty acid glycerol esters – and/or anionic surfactants are present in combination with nonionic surfactants, for example alkyl sulfates of various chain lengths, optionally even several types of alkyl sulfates with various chain lengths in combination with ethoxylated alcohols and/or other nonionic surfactants of the type mentioned above. For example, anionic and nonionic surfactants may also be predominantly accommodated in two different compounds.

In another preferred embodiment of the invention, at least 50% by weight and preferably 60 to 100% by weight of the other constituents are aftertreated before mixing with the disintegrator granules, i.e. are sprayed or powdered under granulating conditions, the water-free aftertreatment being particularly preferred. Preferred liquid constituents include nonionic surfactants and/or polyethylene glycols. However, in another particularly preferred embodiment, the other constituents may also be aftertreated with a water-free melt of nonionic compounds solid at room temperature, more particularly with polyethylene glycols having relative molecular weights above 2,000 and above all between 4,000 and 12,000. As in the case of the disintegrator granules, suitable powdering agents are, above all, fine-

particle zeolites, silicas, sulfates, calcium stearates, phosphates and/or acetates. In another preferred embodiment of the invention, dust and particles smaller than 0.2 mm in size are completely removed before mixing with the disintegrator granules. Applicants assume that this known measure of surface treatment delays dissolution of the particles in the shape/tablet before its actual disintegration and, for this reason, contributes towards the particularly outstanding disintegration properties of the shapes/tablets in the aqueous liquor in the production of shapes in combination with the disintegrator agent granules having a specific particle size distribution.

The invention can also make use of the fact that acidifying agents, such as citric acid, tartaric acid or succinic acid, and also acidic salts of inorganic acids ("hydrogen salts"), for example bisulfates, above all in combination with carbonate-containing systems, can also contribute towards improving the disintegration properties of the shapes. According to the invention, however, these acidifying agents are also used in the form of coarse particles, more particularly granules, which are substantially free from dust and which are adapted in their particle size distribution to the disintegrator granules. The granular acidifying agents may be present in the shapes, for example, in quantities of 1 to 10% by weight.

As already repeatedly mentioned, the shapes according to the invention, more especially the hitherto poorly disintegrating and poorly soluble detergent tablets and bleach tablets, have outstanding disintegration properties. This can be tested, for example, under critical conditions in a normal domestic washing machine bleach/detergent tablet used directly in the wash liquor with the aid of a conventional dispenser, delicates program or coloreds program, washing temperature max. 40°C) or in a glass beaker at a water temperature of 25°C. The carrying out of the corresponding tests is described in the Examples. Under these conditions, the shapes according to the invention not only disintegrate

completely in 10 minutes, the preferred embodiments have disintegration times in the glass beaker test of less than 3 minutes and, more particularly, less than 2 minutes. Particularly advantageous embodiments even have disintegration times of less than 1 minute. Disintegration times of less than 3 minutes in the glass beaker test are sufficient to ensure than the detergent shapes or detergent additive shapes are flushed into the wash liquor from the dispensing compartment of conventional domestic washing machines. In another embodiment, therefore, the present invention relates to washing process in which the detergent shapes are introduced into the wash liquor from the dispensing compartment of a domestic washing machine. The dissolving time of the detergent shapes in the washing machine is preferably less than 8 minutes and more preferably less than 5 minutes.

The actual production of the shapes according to the invention is carried out by initially dry mixing the disintegrator granules with the other constituents and then shaping the resulting mixture, more particularly by compression, into tablets using conventional processes (for example as described in the conventional patent literature on tabletting, above all in the field of detergents of cleaners, more particularly as described in the above-cited patent applications and in the article entitled **"Tablettierung: Stand der Technik" in SÖFW Journal, Vol. 122, pages 1016-1021 (1996)**.

Examples

A granular detergent product with a particle size distribution where more than 90% by weight of the particles were between 0.2 and 2 mm in size with no dust, consisting of 12.9 parts by weight of alkyl benzenesulfonate, 7.4 parts by weight of C_{13-15} alcohol containing on average 5 EO, 0.8 part by weight of soap, 10.5 parts by weight of sodium carbonate, 21 parts by weight of zeolite A, 1.8 parts by weight of sodium silicate (1:3.0), 3 parts by weight of a copolymer typically used in

detergents as a co-builder, 0.5 part by weight of phosphonate, 16 parts by weight of perborate monohydrate, 2.5 parts by weight of enzyme granules, 7 parts by weight of granular bleach activator (tetraacetyl ethylenediamine), 3 parts by weight of foam inhibitor granules based on silicone oil and 8 parts by weight of water, were mixed in accordance with the invention with 4 parts by weight of disintegrator granules (Arbocel® TF-30-HG, a product of Rettenmeier), which was also dust-free with more than 90% by weight of the particles between 0.2 and 2 mm in size, and the resulting mixture was subsequently compressed to form a tablet T1. The tablet press used was a Korsch EK4 press. The tablet obtained had a diameter of 44 mm, a height of 20 mm and a weight of 40 g per tablet.

For comparison, a tablet C1 of the same size and the same weight was produced with 4 parts by weight of microcrystalline cellulose (Avicel® PH-102, a product of FMC, mean particle size 100 µm) instead of the disintegrator granules mentioned.

The hardness of the tablets was measured by deformation to breakage, the force acting on the sides of the tablet and the maximum force which the tablet withstood being determined.

To determine its disintegration rate, the tablet was placed in a glass beaker filled with water (600 ml Düsseldorf municipal water, hardness 16°dH, temperature 30°C) and the time which the tablet took to disintegrate completely in the absence of mechanical action was measured.

The experimental data are set out in Table 1:

Table 1:

Detergent tablets [physical data]

Tablet	T1	C1
Tablet hardness	45 N	44 N
Tablet disintegration	<30 secs.	>60 secs.

CLAIMS

1. A washing- or cleaning-active shape containing at least one disintegrating agent which is capable of increasing the porosity or capillarity of shapes, more particularly tablets, and which has a high adsorption capacity for water, characterized in that the disintegrating agent is present in the shape in granular and optionally in co-granulated form, the granules of disintegrating agent (disintegrator granules) contain at least 20% by weight of the disintegrating agent(s) and the particle size distribution (sieve analysis) is such that at most 1% by weight, preferably less, of dust-fine particles are present and a total of less than 10% by weight of the disintegrator granules is smaller than 0.2 mm in size and at least 50% by weight of the other constituents of the shapes have a particle size of 0.2 to 3 mm.

2. A shape as claimed in claim 1, characterized in that the disintegrator granules contain the disintegrating agent(s) in quantities of 25 to 100% by weight.

3. A shape, more particularly a tablet, as claimed in claim 1, characterized in that at least 90% by weight of the disintegrator granules have a particle size of at least 0.2 mm and at most 3 mm.

4. A shape as claimed in claim 1 or 2, characterized in that the percentage of disintegrator granules smaller than 0.2 mm in size is minimized to 0-5% by weight, at least 90% by weight of disintegrating agent granules preferably having a particle size of at least 0.3 mm and at most 1.6 mm.

5. A shape as claimed in any of claims 1 to 4, characterized in that the disintegrator granules contain the disintegrating agent(s) in quantities of 50 to 100% by weight and, more particularly, at least 70% by weight.

6. A shape as claimed in any of claims 1 to 4, characterized in that the disintegrator granules are present in co-granulated form and the content of disintegrating agent(s) in the disintegrator granules is more than 20% by

weight and less than 70% by weight.

7. A shape as claimed in any of claims 1 to 6, characterized in that it contains disintegrator granules in quantities of 1 to 25% by weight and preferably 2 to 15% by weight, quantities of up to 10% by weight being particularly preferred.

8. A shape as claimed in any of claims 1 to 7, characterized in that at least 70% by weight of the other constituents of the shape have a particle size of 0.2 to 3 mm.

9. A shape as claimed in any of claims 1 to 7, characterized in that it has disintegration times in the glass beaker test (water temperature 25°C) of less than 3 minutes and more particularly less than 2 minutes and dissolving times in a washing machine of less than 8 minutes and more particularly less than 5 minutes.

10. A process for the production of a washing- or cleaning-active shape containing at least one disintegrating agent which is capable of increasing the porosity or capillarity of shapes, more particularly tablets, and which has a high adsorption capacity for water, this disintegrating agent being present in the shape in granular and optionally in co-granulated form, the disintegrator granules containing at least 20% by weight of the disintegrating agent(s) and the particle size distribution (sieve analysis) being such that at most 1% by weight, preferably less, of dust-fine particles are present and a total of less than 10% by weight of the disintegrator granules being smaller than 0.2 mm in size and at least 50% by weight of the other constituents of the shapes having a particle size of 0.2 to 3 mm, characterized in that the disintegrating agent granules are first dry mixed with the other constituents and the resulting mixture is shaped, more particularly by compression, to form tablets.

11. A process as claimed in claim 10, characterized in that at least 70% by weight of the other constituents of the shape have a particle size of 0.2 to 3 mm.

12. A process as claimed in claim 10, characterized in that the other constituents are present in granular form and/or are combined in one compound or several compounds.

13. The use of a disintegrating agent which is capable of increasing the porosity or the capillarity of shapes, more particularly tablets, and which has a high adsorption capacity for water in granular form or in co-granulated form in washing- or cleaning-active shapes, the disintegrating agent granules containing at least 20% by weight of the disintegrating agent(s) and the particle size distribution (sieve analysis) being such that at most 1% by weight of dust is present and less than 10% by weight of the disintegrating agent granules are smaller than 0.2 mm in size.

14. The use of the detergent shape claimed in any of claims 1 to 9 in domestic washing machines.

15. A washing process using the detergent shape claimed in any of claims 1 to 9, characterized in that the detergent shape is introduced into the wash liquor from the dispensing compartment of the domestic washing machine.

NEW CLAIMS

1. A washing- or cleaning-active shape containing at least one disintegrating agent which is capable of increasing the porosity or capillarity of shapes, more particularly tablets, and which has a high adsorption capacity for water, characterized in that the disintegrating agent is present in the shape in granular and optionally in co-granulated form, the granules of disintegrating agent (disintegrator granules) contain at least 20% by weight of the disintegrating agent(s) and the particle size distribution of the disintegrator granules (sieve analysis) is such that at most 1% by weight of dust is present and a total of less than 10% by weight of the disintegrator granules is smaller than 0.2 mm in size.

2. A washing- or cleaning-active shape as claimed in claim 1, characterized in that it contains enzymes.

3. A washing- or cleaning-active as claimed in claim 1, characterized in that it contains bleaching agents.

4. A washing- or cleaning-active shape as claimed in claim 1, characterized in that it contains builders.

5. A washing- or cleaning-active shape as claimed in any of claims 1 to 4, characterized in that at least 50% by weight of the constituents other than the disintegrator granules present in the shape have a particle size of 0.2 to 3 mm.

6. A washing- or cleaning-active shape as claimed in any of claims 1 to 5, characterized in that the disintegrator granules contain the disintegrating agent(s) in quantities of 25 to 100% by weight.

7. A washing- or cleaning-active shape, more particularly a tablet, as claimed in any of claims 1 to 6, characterized in that at least 90% by weight of the disintegrator granules have a particle size of at least 0.2 mm and at most 3 mm.

8. A washing- or cleaning-active shape as claimed in any of claims 1 to 7, characterized in that the percentage of disintegrator granules smaller

than 0.2 mm in size is minimized to 0-5% by weight, at least 90% by weight of disintegrator granules preferably having a particle size of at least 0.3 mm and at most 1.6 mm.

9. A shape as claimed in any of claims 1 to 8, characterized in that the disintegrator granules contain the disintegrating agent(s) in quantities of 50 to 100% by weight and, more particularly, at least 70% by weight.

10. A shape as claimed in any of claims 1 to 8, characterized in that the disintegrator granules are present in co-granulated form and the content of disintegrating agent(s) in the disintegrator granules is more than 20% by weight and less than 70% by weight.

11. A shape as claimed in any of claims 1 to 10, characterized in that it contains disintegrator granules in quantities of 1 to 25% by weight and preferably 2 to 15% by weight, quantities of up to 10% by weight being particularly preferred.

12. A shape as claimed in any of claims 1 to 11, characterized in that at least 70% by weight of the other constituents of the shape have a particle size of 0.2 to 3 mm.

13. A shape as claimed in any of claims 1 to 7, characterized in that it has disintegration times in the glass beaker test (water temperature 25°C) of less than 3 minutes and more particularly less than 2 minutes and dissolving times in a washing machine of less than 8 minutes and more particularly less than 5 minutes.

14. A process for the production of the washing- or cleaning-active shape claimed in any of claims 1 to 13, characterized in that the disintegrating agent granules are first dry mixed with the other constituents and the resulting mixture is shaped, more particularly by compression, to form tablets.

15. A process as claimed in claim 14, characterized in that at least 70% by weight of the other constituents of the shape have a particle size of 0.2 to 3 mm.

16. A process as claimed in claim 14 or 15, characterized in that the other constituents are present in granular form and/or are combined in one compound or several compounds.

17. The use of a detergent shape according to any of claims 1 to 13 in domestic washing machines.

18. The use of a washing- or cleaning-active shape according to any of claims 1 to 13 or claim 17, characterized in that the detergent shape is introduced into the wash liquor from the dispensing compartment of the domestic washing machine.